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The influence study of the number of substituted heteroaryls at the non-K region of pyrene structure on the photophysical properties based on the example of pyrene with 1-decyl-1*H*-1,2,3-triazole motif



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ABSTRACT

The study of the photophysical properties (thermal - thermogravimetric analysis and optical - absorption, emission in the solution and in powder, quantum efficiency of emission and efficient fluorescence lifetime in the solution) with the focus on the influence of the number of substituted 1-decyl-1*H*-1,2,3-triazole groups at the non-K region of pyrene structure. To the best of our knowledge, the investigation of the impact of the number of heteroaryl groups at the non-K region of pyrene is reported for the first time. The obtained results for monosubstituted derivative (**1**) were compared to di- (**2**, **3**) and tetra- (**4**) analogues previously reported by us in the literature. In addition, theoretical studies based on DFT and TD-DFT were performed to support interpreting the experimental results. A strong influence of the number of substituted heteroaryls at the non-K region of pyrene on the photophysical properties was noticed. Theoretical calculations revealed that an increasing number of substituted groups decrease the contribution of pyrene in the creation of frontier orbitals for HOMO from 88 to 72% and LUMO from 91 to 74%, with a simultaneous increase of 1-decyl-1*H*-1,2,3-triazole. The energy gap values follow the same trend, the highest was established for monosubstituted $\Delta E = 3.62$ eV and the lowest for tetrasubstituted $\Delta E = 3.16$ eV. Considering the results of TD-DFT calculations for monosubstituted pyrene, there are no differences in the character of transitions related to absorption and emission in reference to the number of substituted triazole groups at the pyrene core. Therefore, the increasing number of substituted heteroaryls results in red-shifted absorption and emission in the solution and in the solid state (up to 50 nm), increasing the quantum efficiency from 37 to 72% and lower efficient fluorescence lifetime from 9.25 to 2.03 ns.

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1. Introduction

Owing to the fact that pyrene derivatives exhibit interesting photophysical properties makes them still in the great interest of scientists [1–3]. Due to good thermal stability, promising charge-carrier mobility and hole injection ability, pyrene-based π -conjugated derivatives can find applications especially in the area of organic electronics [4–7]. Moreover, the appropriately designed pyrene derivatives can act as NCN-cyclometalating ligands [8–10]. Functionalization of pyrene as a lead structure allows avoiding the formation of the excimers, which is present due to the tendency of unsubstituted pyrene to π -stacking [11]. Multiple systematic stud-

ies presenting the modification of the structure of pyrene at the non-K region (positions 1-, 3-, 6- and 8-) and also at the K-region (positions 4-, 5-, 9-, and 10-) have been already reported; however the studies of the differences between the photophysical properties of derivatives in reference to the number of substituted groups have not been explored.

The synthesis and study of 1,3,6,8-tetrasubstituted by (hetero)aryl groups pyrenes have been comprehensively described in the literature, whereas among the disubstituted at non-K region pyrenes, 1,6- isomers are well-known followed by 1,8- analogues, whereas 1,3-disubstituted pyrenes are relatively unexplored due to the synthetic challenge. Recently, we have reported the comparison of the experimental data for 1,6- and 1,8- isomers and reasonable theoretical results for 1,3,6,8-, 1,6-, and 1,8- isomers, which allowed to obtain the theoretical data of photophysical properties of

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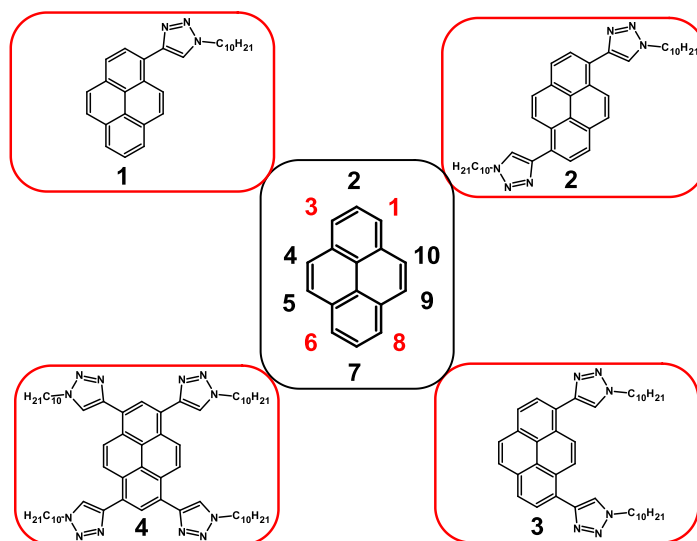


Fig. 1. Structure of the target molecules 1–4.

1,3-disubstituted pyrene by 2-butyl-2*H*-1,2,3,4-tetrazol-5-yl groups [12]. These results indicated that the substitution pattern in disubstituted pyrenes does not affect the properties of molecules.

Furthermore, the study of the substitution pattern of 1,3,6,8-tetrasubstituted pyrene derivatives containing two kinds of groups providing the short axial symmetry or asymmetry was reported [3,13–15]. Compounds with two kinds of units, significantly compound with substitution pattern providing the axial symmetry exhibit more efficient fluorescence compared to 1,3,6,8-tetrasubstituted by the same (hetero)aryl groups pyrenes.

The other conducted study has shown that tetrasubstituted pyrene derivatives, having triazole units at positions 1,8-, and different identical substituents at positions 3,6-, establish the dominance of the triazole units in the pyrene framework; the distinction is even higher in the case of the substitution of the 1,3,6,8 positions by triazoles, but containing two various alkyls what plays a substantial role in elongating the π conjugation of the entire molecule, with significant changes in their photophysical properties [16].

Herein, we present the study of the photophysical properties with the focus on the influence of the number of substituted 1-decyl-1*H*-1,2,3-triazole groups at pyrene structure at the non-K region (Fig. 1).

Compound **1** has already been reported by E. Ramanjaneya Reddy et al. as an isolated model fragment compared to a more elaborate structure in the investigation of the penetration into human breast cancer cells and zebrafish embryos. Still, its photophysical properties were not discussed in detail [17]. Derivatives **2** and **3** were published as intermediates in synthesising 1,3,6,8-tetrasubstituted pyrene derivatives containing two kinds of groups

[13]. Molecule **4** has been reported as NCN-coordinating ligands with potential application in organic electronics [5].

2. Results and discussion

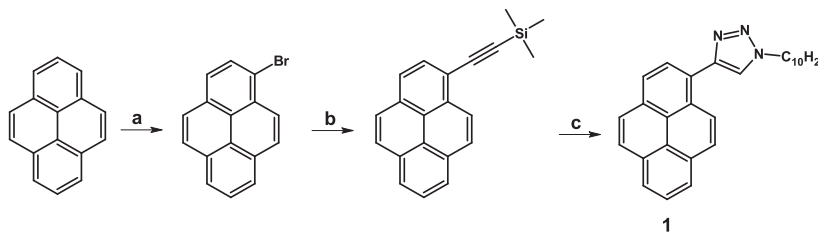
2.1. Synthesis

The assumed synthetic pathway for molecule **1** is presented in Scheme 1. At first, pyrene was brominated by hydrobromic acid in the presence of hydrogen peroxide [18]. This method was definitely more efficient than bromination by *N*-bromosuccinimide in *N,N*-dimethylformamide solution, which resulted in the product with a 10% yield [19]. Then, the Sonogashira cross-coupling reaction between 1-bromopyrene and trimethylsilylacetylene in the presence of catalytic system [Pd(PPh₃)₄]/CuI resulted in the 1-(trimethylsilylethynyl)pyrene [20]. Protected monoethynyl pyrene was used in the [Cu]-mediated cycloaddition reaction with decyl azide, resulting in 1-decyl-4-(pyren-1-yl)-1*H*-1,2,3-triazole (**1**) with a 74% yield.

The structures of compound **1** and intermediates were confirmed by the ¹H and ¹³C NMR and in the case of **1** by the MS spectrometry presented in Experimental Section and Supplementary Information. The synthesis of molecules **2–4** was not performed because they are already reported in previously published by us protocols [5,13].

2.2. Thermal properties

Thermal properties of **1** have been examined using thermogravimetric analysis up to 900 °C under a nitrogen atmosphere.



Scheme 1. Synthesis of 1-decyl-4-(pyren-1-yl)-1*H*-1,2,3-triazole. Reagents and conditions:

(a) HBr, H₂O₂, Et₂O, MeOH, room temp., 12 h, (Yield = 82%); (b) trimethylsilylacetylene, [Pd(PPh₃)₄], CuI, *i*-Pr₂NH, THF, 76 °C, 16 h, (Yield = 92%); c) decyl azide, KF, CuSO₄·5H₂O, sodium ascorbate, pyridine, *t*-BuOH, H₂O, room temp. (25 °C), 24 h, (Yield = 74%).

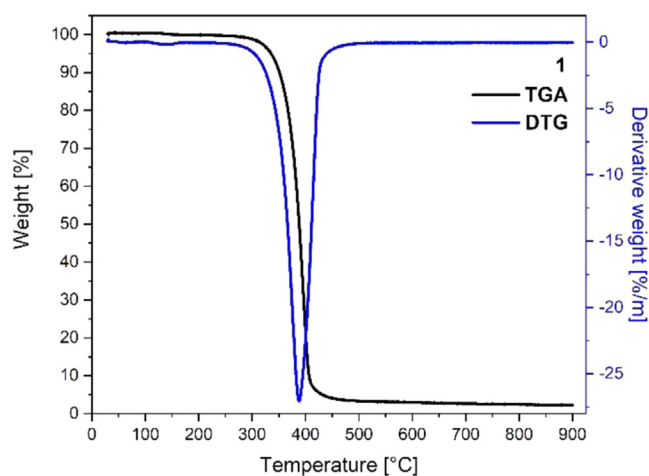


Fig. 2. (a) TGA and DTG curve of pyrene derivative 1.

Table 1
Thermal properties of pyrene derivatives.

	TGA				ref.
	T _{5%} [°C]	T _{10%} [°C]	T _{max} [°C]	Char residue at 900°C [%]	
1	335	351	388	2	-
2	375	385	411	4	[13]
3	324	357	414	1	[13]
4	303	365	409	15	[5]

T_{5%}, T_{10%} – the temperature of 5% and 10% weight loss
T_{max} – the maximum decomposition rate from DTG thermograms

The monosubstituted pyrene compound can be characterized as a thermal stable molecule with a high temperature of 5% and 10% weight loss, 335 °C and 351 °C, respectively (Fig. 2). Comparing obtained results with the pyrene derivatives containing two (**2**, **3**) and four (**4**) substituted groups, already described in the literature, demonstrated that the most stable are molecules with two substituted groups, whereas 1-decyl-4-(pyren-1-yl)-1*H*-1,2,3-triazole is the least thermally stable molecule among studied group (Table 1).

2.3. Quantum chemical calculations

To achieve a deep insight and understand the influence of the number of substituted heteroaryls at the non-K region of pyrene structure on the photophysical properties, the quantum chemical calculations of compound **1** were performed using DFT and TD-DFT methods, as implemented in the Gaussian 16 package [21], and compared with literature data of di- (**2**, **3**) and tetrasubstituted pyrenes (**4**). All calculations were performed with the polarizable continuum model (PCM) [22]. All orbitals were computed at an isovalue of 0.03 e/bohr³. TD-DFT method with B3LYP/6-31G(d,p) and CAM-B3LYP/6-31G(d,p) level was used to calculate the wavelengths of absorption and emission, the bands and their character were established using GaussSum software [23]. The optimized geometric structures at the B3LYP/6-31G(d,p) level with the selected molecular electron density contours, energies, and contribution in their creation (pyrene/1-decyl-1*H*-1,2,3-triazole) (HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1, LUMO+2) of **1** are displayed in Table 2.

It was found that all presented molecular orbitals are mainly localized on the pyrene core. Frontier orbitals are delocalized on pyrene in 88% (HOMO) and 91% (LUMO), whereas the contribution of 1-decyl-1*H*-1,2,3-triazole is 12% and 9%, respectively. An increasing number of substituted groups decrease the contribution of pyrene in the creation of frontier orbitals with a simultaneous increase of 1-decyl-1*H*-1,2,3-triazole as follows HOMO: **2** (80/20), **3** (81/19), **4** (72/28), and LUMO: **2** (84/16), **3** (85/15), **4** (74/24) [13].

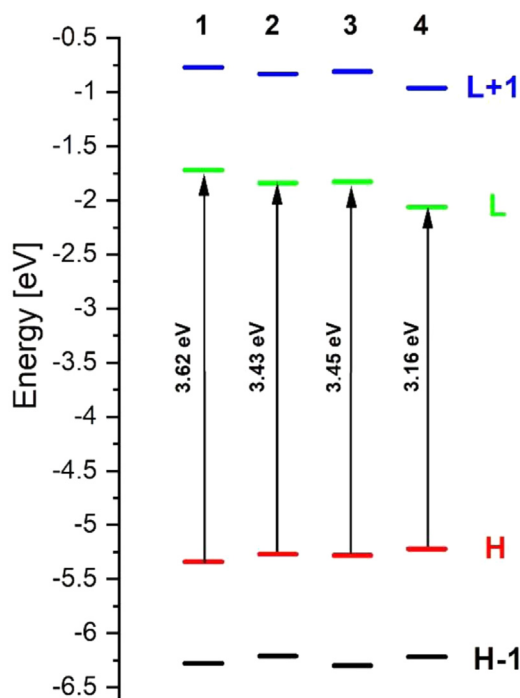


Fig. 3. Energy gaps (ΔE) of 1–4.

The energy gap values follow the same trend, the highest was established for **1** ($\Delta E = 3.62$ eV) containing one substituted triazole motif (Fig. 3).

Considering the results of TD-DFT calculations for molecule **1** (Table 3), there are no differences in the character of transitions related to absorption and emission bands in reference to the number of substituted triazole groups at the pyrene core. The lowest energetic absorption band and emission band can be described as HOMO→LUMO transitions, which was also previously noticed for di- (**2**, **3**) and tetrasubstituted (**4**) analogues [5,13]. It may be expected that a higher number of substituted heteroaryl groups (triazole) will result in a bathochromic spectrum shift.

2.4. Photophysical properties

The photophysical properties of 1-decyl-4-(pyren-1-yl)-1*H*-1,2,3-triazole (**1**) were investigated in the dichloromethane solution and in the solid state. The obtained data were compared with the reported in the literature data for di- (**2**, **3**) and tetrasubstituted (**4**) pyrenes, the corresponding data of investigation in the solution are presented in Fig. 4 and Table 4.

Compounds **1–4** possess three absorption bands which are typical for unsubstituted pyrene [24]. The absorption maxima of compounds **1–4** are in the range of 250–440 nm and are in good agreement with the excitation spectrum. 1-Decyl-4-(pyren-1-yl)-1*H*-1,2,3-triazole possessing one substituent exhibit $S_0 \rightarrow S_1$ transition in dichloromethane solution shifted to shorter wavelength by around 10 and 40 nm compared to di- (**2**, **3**) and tetrasubstituted (**4**) pyrene derivatives, respectively [5,13], pointing out the smaller conjugation of π -electron in 1-decyl-4-(pyren-1-yl)-1*H*-1,2,3-triazole (**1**) by the presence of one unit in pyrene moiety (Fig. 4a). On the other hand, the intensity of the high energy transition for compounds **1–4** decreases with increasing triazole units. Moreover, compounds **2** and **3** having two triazole units differing by substituent position, possess the same absorption shape and maxima.

Compound **1** in dichloromethane shows an emission band at 388 nm with the shoulder at around 400 nm, which is hyp-

Table 2
Molecular orbitals calculated at B3LYP/6-31G(d,p) level, their energies, and contribution in their creation (pyrene/1-decyl-1H-1,2,3-triazole) for molecule **1**.

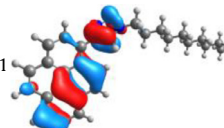
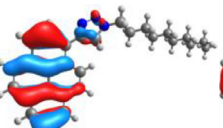
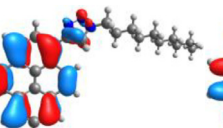
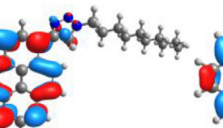
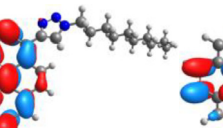
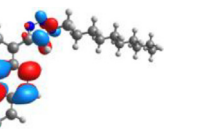
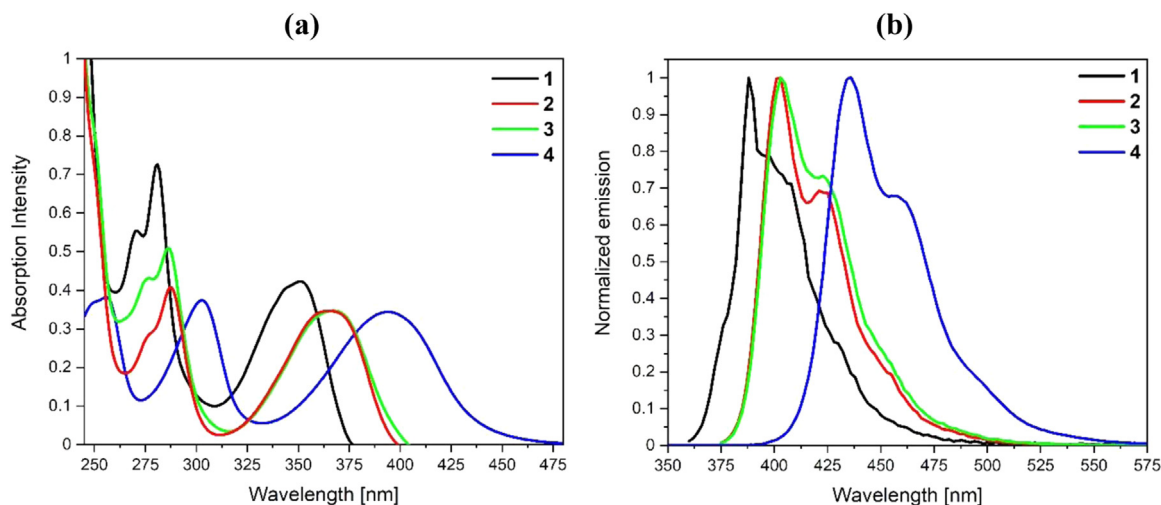
	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2
						
	61/39 -6.92 eV	92/8 -6.28 eV	88/12 -5.34 eV	91/9 -1.72 eV	97/3 -0.77 eV	82/18 -0.23 eV

Table 3
The calculated absorption and emission wavelengths by the TD-DFT method (6-31G(d,p)/B3LYP or CAM-B3LYP) with oscillator strengths for **1**.

	Calculated wavelengths [nm](oscillator strengths)	Transitions (contribution)	Calculated wavelengths [nm](oscillator strengths)	Transitions(contribution)
1 absorption	B3LYP		CAM-B3LYP	
	365.54 (0.6009)	HOMO→LUMO (95%)	325.84 (0.6920)	HOMO→LUMO (95%)
	281.48 (0.4565)	H-1→LUMO (48%), HOMO→L+1 (41%)	250.25 (0.7002)	H-1→LUMO (51%), HOMO→L+1 (44%)
	248.87 (0.1608)	HOMO→L+4 (51%), H-4→LUMO (17%), H-1→L+1 (13%)	227.71 (0.3554)	H-1→L+1 (27%), H-3→LUMO (26%), H-2→LUMO (25%)
	234.42 (0.4590)	H-1→L+1 (63%), HOMO→L+4 (11%)	222.29 (0.1109)	HOMO→L+4 (29%), HOMO→L+3 (13%), H-2→LUMO (10%), H-1→L+1 (10%), H-1→L+2 (10%)
229.08 (0.1603)	H-2→L+1 (23%), H-5→LUMO (21%), H-3→L+1 (14%), HOMO→L+5 (11%)	216.93 (0.6618)	H-1→L+1 (51%), HOMO→L+4 (21%)	
1 emission	431.99 (0.8604)	HOMO→LUMO (99%)	401.52 (0.9765)	HOMO→LUMO (98%)

**Fig. 4.** Absorption (a) and emission (b) spectra of pyrene derivatives **1–4** recorded in dichloromethane solution (CH_2Cl_2).

spectrally shifted compared to that of pyrene itself [25]. The increasing π -conjugation length and the increasing number of triazole substituents in pyrene derivatives reflect on their emission spectra similarly to absorption spectra. The monosubstituted 1-decyl-4-(pyren-1-yl)-1H-1,2,3-triazole displays a progressively blue-shifted emission spectrum compared to di- (**2** and **3**) and tetrasubstituted pyrene **4** derivatives in dichloromethane solutions [5,6,13]. The quantum efficiency of emission for 1-decyl-4-(pyren-1-yl)-1H-1,2,3-triazole (**1**) was from 26 to 35% lower than for di- and tetrasubstituted pyrenes **2–4** (Table 4). The quantum efficiency of pyrene **1–4** derivatives gradually increases with the number of substituents, confirming the effect of extending the π -conjugation. 1-Decyl-4-(pyren-1-yl)-1H-1,2,3-triazole (**1**) ex-

hibits similarly to the **2–4** pyrene derivatives, biexponential decay in the dichloromethane solution (Table 4). Interestingly, the luminescence decay curves for **2–4** pyrene derivatives are nearly monoexponentially fitted with the second decay share, only slightly influencing the efficient lifetime. In the case of compound **1**, decays consist of two elements implying emission from more than one excited state (Fig. 5).

Intriguingly, the non-radiative processes rate constant k_{nr} for compound **1** is more significant than its radiative processes rate constant k_r , in contrast to compounds **2–4**, explaining the higher quantum yield of the latter.

Compound **1** and pyrene derivatives **2–4** reported in the literature were found to be luminescent in the solid state with

Table 4
Photophysical and optical data recorded in the dichloromethane solution ($c = 10^{-5}$ mol/L) for pyrene derivatives **1–4**.

	λ_{abs} [nm] ($\epsilon/10^5$ M $^{-1}$ cm $^{-1}$)	PL λ_{em} [nm] / Stokes shift [cm $^{-1}$]	Φ [%]	τ [ns] (weight %)	$k_r \cdot 10^6$ [s $^{-1}$] ^[a]	$k_{\text{nr}} \cdot 10^6$ [s $^{-1}$] ^[a]	χ^2	$E_{\text{g, opt}}$ [eV] ^[b]	ref
1	271 (0.55), 281 (0.73), 351 (0.42)	388/2717	37	9.25 [3.04 (33.99) 13.69 (60.01)]	40.00	68.11	0.994	3.19	-
2	277 (0.29), 287 (0.41), 365 (0.35)	403/2584, 421/3645	64	3.72 [0.04 (12.37) 4.24 (87.63)]	171.61	97.20	0.962	3.09	[13]
3	277 (0.43), 286 (0.51), 367 (0.35)	403/2434, 423/3607	63	2.37 [0.03 (18.07) 2.89 (81.93)]	267.38	154.56	1.023	3.08	[13]
4	256 (0.38), 302 (0.37), 391 (0.34)	436/2640, 458/3741	72	2.03 [0.15 (10.52) 2.25 (89.48)]	354.68	137.93	1.073	2.85	[5]

^[a] Radiative (k_r) and non-radiative (k_{nr}) decay rates assuming that emission excited states are produced with unit efficiency are estimated using the following equations: $k_r = \Phi_{\text{em}}/\tau$; $k_{\text{nr}} = (1-\Phi_{\text{em}})/\tau$

^[b] $E_{\text{g, opt}} = 1241/\lambda_{\text{em}}$

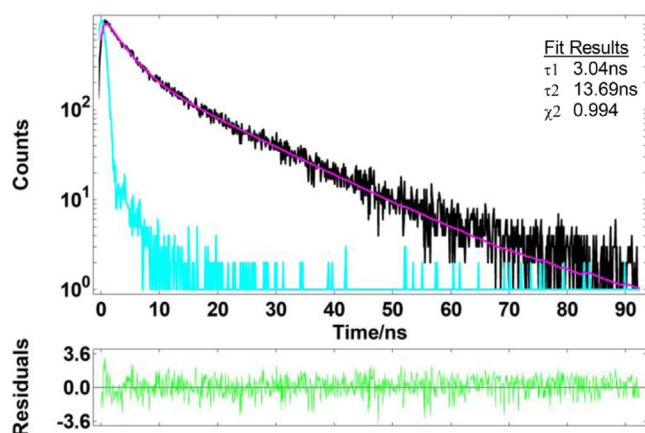


Fig. 5. Time decay spectrum of 1-decyl-4-(pyren-1-yl)-1H-1,2,3-triazole (**1**).

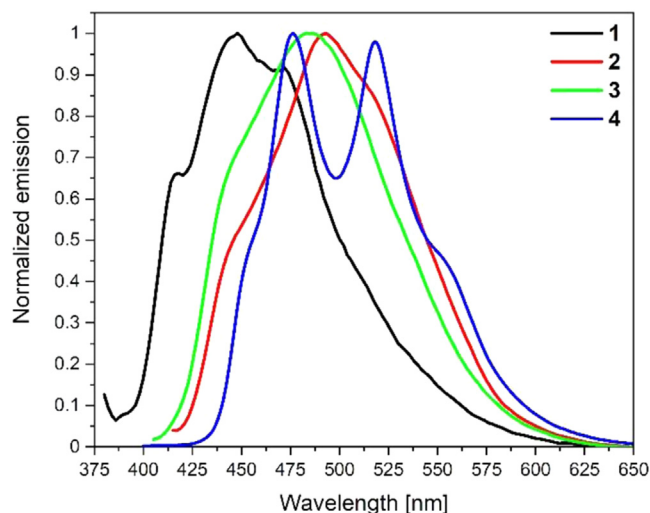


Fig. 6. The emission spectra recorded in powder of pyrene derivatives **1–4**.

maxima in the range of 418–518 nm (Fig. 6, Table 5) [5,13]. The excitation spectrum of 1-decyl-4-(pyren-1-yl)-1H-1,2,3-triazole (**1**) in the solid state is more structural but without change of the energy range of the transitions (Fig. S1). In the solid state, all pyrene derivatives **2–4** display significantly red-shifted and broadened emission bands compared to those in solution, which are the mutual features of organic luminophores in the solid state result-

ing from numerous intermolecular interactions. A similar tendency to the red shift of emission maxima with the enhancement of substituents in solution is observed in the solid state; compound **4** possesses two emission bands in the solid state, suggesting two various aggregate sites.

The next part of the study investigated the dipole moment changes in the ground state and excited state (triplet state) in compound **1** in solvents of different polarities to consider the solvatochromic effect (Table 6). For compound **1**, the marginal deviation of the dipole moment value between the ground and the excited state with an increase of solvent polarity was observed, pointing out the lack of solvatochromic effect in compound **1**. This observation is consistent with the negligible positive solvatochromic effect shown in the emission spectra of similarly substituted pyrene derivatives [26,27].

The presented results indicate the considerably sensitive substitution patterns of pyrene derivatives **1–4**. The absorption and emission spectral range of **1–4** are significantly red-shifted from one to four units in the pyrene. Moreover, the quantum yield holds the same tendency. Interestingly photophysical parameters of disubstituted derivatives **2** and **3** are very similar, indicating the same character of the excited state.

3. Materials and methods

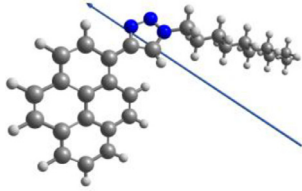
All reagents were purchased from commercial suppliers and used as received. NMR spectra were measured in deuterated chloroform using Bruker Avance 400 MHz (^1H and ^{13}C NMR). High-resolution mass spectrometry (HRMS) measurement was conducted using Mass Spectrometer QTOF (Impact HD, Bruker). Thermogravimetric analysis (TGA) was carried out using Pyris 1 TGA Perkin-Elmer. Melting point was measured by Electrothermal IA9300 Digital Melting Point Apparatus. UV-Vis spectrum was measured using Perkin-Elmer Lambda Bio 40 UV-Vis spectrophotometer at room temperature with a conventional 1.0 cm quartz cell. The emission and excitation spectra were measured by using the spectrophotometer Hitachi F-7000. The quantum yield of fluorescence was determined by the absolute method at room temperature, using the integrating sphere with solvent as a blank (FLS-980 spectrophotometer). The time-resolved measurement has been prepared at optically diluted solutions at room temperature using the time-correlated single-photon counting methods on the FLS-980 spectrophotometer.

Synthesis of 1-decyl-4-(pyren-1-yl)-1H-1,2,3-triazole – In a 100 mL round-bottom flask, 1-(trimethylsilylethynyl)pyrene (0.40 g, 1.34 mmol), decyl azide (0.30 g, 1.64 mmol), *tert*-butanol

Table 5
Optical data recorded in powder for pyrene derivatives **1–4**.

	λ_{exc} [nm]($\epsilon/10^5$ M ⁻¹ cm ⁻¹)	PL λ_{em} [nm] /Stokes shift [cm ⁻¹]	$E_{g, opt}$ [eV] ^[a]	ref
1	283, 307, 322, 336, 367	418/3324, 448/4926, 472/6061	2.63	-
2	284, 326, 364	493/7189	2.52	[13]
3	276, 326, 366	483/6619	2.57	[13]
4	278, 329, 370	476/5992, 518/7695	2.39	[5]

^[a] $E_{g, opt} = 1241/\lambda_{em}$ **Table 6**
Calculated dipole moment B3LYP/6-31G(d,p) for molecule **1**.

Solvent	ground state (μ_g) [D]	excited state (μ_e) [D]	$\Delta\mu$ [D]
	4.87	4.82	-0.05
PhCH ₃	5.03	4.98	-0.05
CH ₂ Cl ₂	5.42	5.39	-0.03
ACN	5.96	5.94	-0.02
DMSO	5.99	5.97	-0.02

(35 mL) and water (35 mL) were placed. The mixture was bubbled with argon, and then CuSO₄·5H₂O (0.41 g, 1.64 mmol), sodium ascorbate (0.32 g, 1.64 mmol), KF (0.10 g, 1.64 mmol), and pyridine (1.0 mL) were added. The mixture was stirred at room temperature for 24 h. Then, dichloromethane (20 mL) and a 5% solution of ammonia (10 mL) were added, and the mixture was stirred for 30 min. The mixture was extracted with water (25 mL) and dichloromethane (2 × 25 mL). The combined organic layers were dried with anhydrous MgSO₄, and the volatile fractions were evaporated. The crude product was purified by column chromatography (silica gel; CH₂Cl₂, ethyl acetate). Product was obtained as yellow-orange solid in 74% (0.41 g), mp 108–110 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.71 (d, J = 9.3 Hz, 1H), 8.24 (t, J = 7.9 Hz, 1H), 8.20 (dd, J = 7.7, 3.6 Hz, 3H), 8.11 (dd, J = 7.6, 5.2 Hz, 1H), 8.09 (d, J = 2.3 Hz, 2H), 8.02 (t, J = 7.6 Hz, 1H), 7.92 (s, 1H), 4.50 (t, J = 7.3 Hz, 2H), 2.09–1.98 (m, 2H), 1.49–1.37 (m, 4H), 1.32 (d, J = 28.8 Hz, 10H), 0.88 (t, J = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 147.5, 131.6, 131.4, 131.1, 128.7, 128.3, 128.2, 127.9, 127.5, 127.3, 126.2, 125.6, 125.5, 125.4, 125.2, 125.0, 124.9, 122.8, 50.7, 32.0, 30.59, 29.6, 29.6, 29.4, 29.2, 26.8, 22.8, 14.2. HRMS (ESI): m/z calcd. for C₂₈H₃₂N₃ [M + H]⁺ 410.2591; found 410.2596.

4. Conclusion

A strong influence of the number of substituted heteroaryls at the non-K region (positions 1,3,6,8) of pyrene on the photo-physical properties was studied based on mono-, di-, and tetra-substituted pyrene by 1-decyl-1H-1,2,3-triazole groups. 1-Decyl-4-(pyren-1-yl)-1H-1,2,3-triazole (**1**) was synthesized and characterized in terms of thermal and optical properties, and the obtained results were confronted with previously reported by us data for di- and tetra- analogues. The substitution (mono-, di-, and tetra-) does not significantly influence on the thermal stability of molecules, the most stable are molecules with two substi-

tuted groups, whereas monosubstituted is the least thermally stable molecule with a still high temperature of 5% and 10% weight loss, 335 and 351 °C, respectively. Furthermore, theoretical calculations revealed that an increasing number of substituted groups decrease the contribution of pyrene in the creation of frontier orbitals for HOMO from 88 to 72% and LUMO from 91 to 74%, with a simultaneous increase of 1-decyl-1H-1,2,3-triazole. The energy gap values follow the same trend, the highest was established for monosubstituted $\Delta E = 3.62$ eV and the lowest for tetrasubstituted $\Delta E = 3.16$ eV. Considering the results of TD-DFT calculations for monosubstituted pyrene, there are no differences in the character of transitions related to absorption and emission in reference to the number of substituted triazole groups at the pyrene core. The increasing π -conjugation length and the increasing number of triazole substituents in pyrene derivatives reflect on their emission spectra similarly to absorption spectra which are red-shifted in the solution and in the solid state. All pyrene derivatives display significantly red-shifted and broadened emission bands in the solid state compared to those in the solution. The increase of the quantum efficiency from 37 to 72% and lower efficient fluorescence lifetime from 9.25 to 2.03 ns from monosubstituted to tetrasubstituted. Dipole moment changes in the ground state and excited state (triplet state) in monosubstituted derivative in solvents of different polarities show the marginal deviation pointing out the lack of solvatochromic effect. The presented results indicate the considerably sensitive substitution patterns of pyrene derivatives.

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Declaration of Competing Interest

The authors declare no conflict of interest.

CRediT authorship contribution statement

Dawid Zych: Conceptualization, Methodology, Investigation, Data curation, Writing – original draft, Writing – review & editing. **Aneta Slodek:** Investigation, Data curation, Writing – original draft, Writing – review & editing. **Norbert Krzyżanowski:** Data curation.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.molstruc.2022.133797](https://doi.org/10.1016/j.molstruc.2022.133797).

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